

UNITED STATES PATENT APPLICATION

OF

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For

CROSSLINKED POLYVINYL ALCOHOL FIBER

AND METHOD FOR PRODUCING THE SAME

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BACKGROUND OF THE INVENTION

Field of the Invention

[01] The present invention relates to crosslinked polyvinyl alcohol fiber and method for producing the same, and more particularly, to crosslinked polyvinyl alcohol fiber, in which PVA resin having a degree of polymerization of more than 1,000 and a degree of saponification of more than 97.0 mol% is dissolved in dimethyl sulfoxide (hereinafter, referred to as DMSO), the solution is subjected to dry and wet gel spinning using methanol as a coagulation solution, drawn and thermally treated, the resulting polyvinyl alcohol drawn yarn with 500-3,000 deniers is twisted to produce a cabling yarn, the cabling yarn is plied into a 2-ply or 3-ply yarn to produce a raw cord, the raw cord is wound on a bobbin for crosslinking and crosslinked in an aqueous crosslinking solution containing an aromatic aldehyde compound and an acid catalyst. Moreover, the present invention relates to a crosslinker-introducing apparatus, which is used in the above method and can effectively induce the crosslinking reaction of the wound raw cord.

Background of the Related Art

[02] A polyvinyl alcohol fiber (hereinafter, referred to as PVA) shows superior strength and modulus to general purpose fibers, such as polyamide, polyester, and polyacrylonitrile fibers, and is very excellent in particularly adhesion, water dispersibility, alkaline resistance and chemical resistance. Thus, it is used as materials of various industrial fields.

[03] Recently, PVA is also used as a reinforcement material for concrete, cement, rubber, plastic and the like, and studied and developed as a material with high applicability to new fields.

[04] Till now, various methods for producing a high-strength PVA fiber were proposed.

[05] US Patent No. 4,440,711 discloses a method for preparing a high-strength PVA fiber using a gel spinning technique (US patent No. 4,698,194) in which high-molecular weight polyethylene as a raw material is drawn to high draw ratio to produce the high-strength fiber. The gel spinning technique is a general method for producing the high-strength fiber, in which a polymer compound is mixed with solvent to prepare a uniform solution, and then, the solution is drawn to high draw ratio while suitably adjusting phase separation and gelling occurring in a spinning process.

[06] Furthermore, a technology on method for producing PVA fiber having more excellent physical properties using this gel spinning technique was also known.

[07] Japanese patent laid-open publication No. Heisei 7-109616 discloses a method for producing a PVA multifilament fiber with a tensile strength of at least 22 g/denier, an initial modulus of at least 440 g/denier and a yarn CV of less than 5%, in which dry and wet spinning processes are performed using a spinneret with an orifice diameter of 0.1-1 mm and an orifice length-to-diameter (L/D) ratio of 3-20.

[08] However, although the PVA fiber produced by this method has excellent mechanical properties, the PVA resin is dissolved in hot water with a high temperature above 100 °C or has reduced mechanical properties, due to the hydrophilicity of PVA resin itself. Thus, it has many limitations for use in applications, such as tire cords which have the biggest market among the industrial fibers.

[09] Although a very small amount of water is present in the inside of a tire, excess water can flow into the tire when the tire gets damaged. Also, when the tire temperature is increased to 130 °C as a result of high-speed running of automobile, the water is thermally hydrated to cause damages to the PVA fiber, so that the stability of automobiles is endangered.

Thus, the PVA fiber according to the prior art could not be used as a tire reinforcement material without anxiety.

[10] Also, since the high crystallinity of the PVA fiber results in a reduction in fatigue resistance when it is used for tire cords, this problem needs to be solved.

[11] To improve hot water resistance and fatigue resistance, various methods were developed in which PVA with a high degree of polymerization is spun, thermally drawn to high draw ratio, thermally treated, acetalized and crosslinked by an acid catalyst. However, it is difficult to use the PVA fibers as filaments for industrial purpose. And, when the PVA resin produced by such methods is used in hot water above 130 °C, a problem occurs.

[12] Particularly in the crosslinking technology proposed in the prior art, a crosslinker is added to a spinning dope before a drawing process or during an extraction or oil-treating process.

[13] Korean patent registration No. 210727 discloses a method for producing a polyvinyl alcohol fiber with excellent hot water resistance, in which a yarn containing an acetal compound of aliphatic dialdehyde as a crosslinker is prepared, subjected to dry heat drawing and crosslinked by an acid.

[14] Korean patent laid-open publication No. 96-41438 discloses a method for producing a polyvinyl alcohol fiber with excellent hot water resistance, in which a yarn containing an

ammonium sulfate crosslinker is subjected to dry heat drawing and then crosslinked.

[15] As described above, in the crosslinking technologies proposed till now, the crosslinker is added to the spinning dope before the drawing process or in the extraction or oil-treating process. In such prior crosslinking methods, when subjected to thermal drawing at a high temperature above 200 °C, the crosslinker contained in the PVA undrawn yarn cause crosslinking reaction to reduce drawability, or the crosslinker with low boiling point is volatilized to reduce crosslinking efficiency. Thus, the crosslinker hardly has a hot water resistance above 130 °C.

[16] Furthermore, the crosslinking treatment methods as described above have a problem in that, since crosslinking treatment is performed by simply dipping a bobbin wound with a undrawn yarn into the crosslinker, a portion of the undrawn yarn wound inside the bobbin is not impregnated with the crosslinker, and thus, incompletely crosslinked, or the outer side of the undrawn yarn wound on the bobbin is crosslinked at a significantly different level from the inside of the undrawn yarn.

SUMMARY OF THE INVENTION

[17] An object of the present invention is to provide a crosslinked polyvinyl alcohol fiber, in which a polyvinyl alcohol

drawn yarn with 500-3,000 deniers is twisted to form a cabling yarn, the cabling yarn is plied into a 2-ply or 3-ply yarn to prepare a raw cord, the raw cord wound on a bobbin for crosslinking reaction is crosslinked in an aqueous crosslinking solution containing an aromatic aldehyde compound and an acid catalyst.

[18] Another object of the present invention is to provide a crosslinker-introducing apparatus, which is used in the above inventive method and allows the polyvinyl alcohol fiber to have excellent hot water resistance and high strength.

[19] To accomplish the above objects, according to one aspect of the present invention, there is provided a crosslinked raw cord which is produced by a method comprising the steps of: (A) spinning polyvinyl alcohol having a degree of polymerization of 1,000-7,000 according to a dry and wet spinning technique or a wet spinning technique, drawing the undrawn yarn to high draw ratio, and thermally treating the drawn yarn; (B) twisting the polyvinyl alcohol drawn yarn to prepare a cabling yarn, and plying the cabling yarn into a 2-ply or 3-ply yarn to produce a raw cord; and (C) crosslinking the raw cord by dipping it into the crosslinker.

[20] To accomplish the above objects, according to one aspect of the present invention, there is provided a crosslinker-introducing apparatus comprising a cylindrical bobbin which has a

hollow formed therein, a plurality of through-holes formed on the circumferential surface and on which a raw cord is wound and a closed container which is charged with the crosslinker and provided in such a manner that the bobbin for crosslinking is dipped in the crosslinker.

[21] To accomplish the above objects, according to one aspect of the present invention, there is provided a crosslinked raw cord which is produced by a method comprising the steps of: (A) dissolving polyvinyl alcohol having a degree of polymerization of 1,000-7,000 and a degree of saponification of more than 97.0 mol% in dimethyl sulfoxide, spinning the solution according to a dry and wet spinning technique or a wet spinning technique, drawing the undrawn yarn to high draw ratio, and thermally treating the drawn yarn; (B) twisting the polyvinyl alcohol drawn yarn to prepare a cabling yarn, and plying the cabling yarn into a 2-ply or 3-ply yarn to produce a raw cord; and (C) crosslinking the raw cord using the crosslinker-introducing apparatus described above in an aqueous crosslinking solution containing an aromatic aldehyde compound and an acid catalyst while adding alcohol to the aqueous crosslinker solution.

[22] Preferably, the alcohol added to the aqueous crosslinking solution in the step (C) is methanol.

[23] Preferably, the content of the alcohol added to the aqueous crosslinking solution in the step (C) is 1-30 wt%.

[24] Preferably, the content of the aromatic aldehyde compound crosslinked to the raw cord in the step (C) is 0.1-5.0 wt%.

[25] Preferably, the aromatic aldehyde crosslinked to the raw cord in the step (C) is terephthalaldehyde (TDA).

[26] Preferably, the acid catalyst is used in the crosslinking of the raw cord in the step (C).

[27] Preferably, the acid catalyst used in the step (c) is acetic acid.

[28] To accomplish the above objects, according to one aspect of the present invention, there is provided a treated cord for tire cords, which is produced by treating the crosslinked raw cord described above with a dipping solution (RFL) and has the following physical properties: (1) a breaking load of 20.0-50.0 kgf; (2) a fineness of 1,000-6,000 deniers; (3) hot water resistance of at least 130 °C; and (4) a fatigue resistance of at least 80%.

[29] The crosslinker which is used in the present invention is preferably an aldehyde compound capable of crosslinking with the hydroxy group of PVA, and the aldehyde compound preferably has two or more aldehyde groups in order to increase crosslinking efficiency. The aldehyde compound is more preferably an aromatic compound which infiltrates only into the non-crystalline region of the fiber.

[30] Examples of this aromatic aldehyde compound include terephthaldicarboxaldehyde (TDA), isophthaldicarboxaldehyde (IDA) and naphthaldicarboxaldehyde (NDA), and a mixture of two or more thereof.

[31] As the aromatic aldehyde compound, terephthaldicarboxaldehyde (TDA) is preferably used in the present invention.

[32] It is the key technical point of the present invention that the aromatic aldehyde capable of infiltrating only into the non-crystalline region of the drawn yarn is used as the crosslinker. Since the aromatic aldehyde is mainly infiltrated only into the non-crystalline region of the yarn, the tenacity of the drawn yarn can be prevented from being reduced due to the crosslinker.

[33] The most important characteristic of the present invention is a crosslinking process. In general crosslinking, there is used a method wherein the crosslinker is dissolved in an organic solvent in an extraction process in order to infiltrate the crosslinker into the inside of the fiber. However, this crosslinker within the undrawn fiber causes a reduction in drawability in a thermal drawing step at high temperature above 200 °C, so that the drawn yarn does not have sufficient hot water resistance and fatigue resistance. The crosslinker used in the

extraction process makes organic solvent recovery difficult and thus an entire process difficult.

[34] For this reason, in the present invention, in order to increase crosslinking efficiency and to prevent fiber damage, the twisted PVA raw cord is crosslinked after it is infiltrated with the crosslinker. This gives a high-strength PVA fiber having a hot water resistance above 130 °C and a fatigue resistance of at least 80%.

[35] A key technical point in the present invention is that the raw cord is crosslinked in a crosslinking solution containing an aromatic aldehyde compound and an acid catalyst while adding alcohol to the aqueous crosslinking solution. The addition of alcohol to the crosslinking solution allows significant prevention of reduction in tenacity.

[36] Hereinafter, the producing method of the PVA fiber will be described in detail.

[37] PVA has a degree of polymerization of about 1,000-7,000, and preferably 1,500-4,000. At a degree of polymerization lower than 1,000, it is difficult to form it into fibers, and at a degree of polymerization higher than 7,000, it has so high viscosity to reduce spinning processability. Since the high-strength PVA fibers which are mostly used in the industrial material field need to have hot water resistance, PVA with a saponification degree of more than 97.0 mol% is used. As the

organic solvent, ethylene glycol, glycerin, and DMSO may be used, but DMSO is suitable for its highest solubility for PVA. This DMSO is preferably purified to a water content of less than several tens ppm before use.

[38] The concentration of the PVA dope is adjusted such that its viscosity is preferably in a range of 50-4,000 poise, and more preferably 500-3,000 poise in order to obtain excellent physical properties. At a viscosity below 50 poise, it is difficult to form the PVA dope into a fiber, and at a viscosity above 4,000 poise, fiber spinnability is reduced.

[39] A coagulation bath has a temperature of -30 to 30 °C for possible spinning, and preferably -10 to 10 °C for the formation of uniform gel. If the temperature of the coagulation bath is below -30 °C, PVA spinning dope may be frozen. If the temperature of the coagulation bath is higher than 30 °C, gel formation becomes impossible so that spinnability will be reduced.

[40] A method for producing a PVA fiber is performed by a dry spinning technique, a wet spinning technique, and a dry and wet spinning technique, but in a method for producing a high-strength PVA fiber where a drawing process with high draw ratio is required, the dry and wet spinning technique is preferred. For the production of a PVA filament, the air-gap in the dry and wet spinning technique may be 5-200 mm, but for thermal drawing to high draw ratio, a narrow air-gap of 5-50 mm is preferred. At

an air-gap below 5 mm, workability will be reduced. On the other hand, at an air-gap above 200 mm, crystallinity is greater than gelling to make the thermal drawing at high draw ratio impossible, and also the fusion between fibers on a nozzle section occurs to reduce productivity.

[41] In the producing method of the high-strength PVA fiber, the drawing process is very important for high strength and improved hot water resistance. Examples of a heating manner in the drawing process include a hot air heating manner and a roller heating manner. In the roller heating manner, a filament is in contact with the roller surface such that the fiber surface is liable to be damaged. Thus, the hot air heating manner is more effective for the production of the high-strength PVA fiber. The heating temperature may be 140-250 °C, and preferably 160-230 °C. At a heating temperature below 140 °C, molecular chains will not sufficiently move to make the thermal drawing at high draw ratio impossible, and above 250 °C, PVA is liable to be decomposed to cause a reduction in physical properties.

[42] Furthermore, in the PVA fiber used as a tire cord among industrial materials, high strength and fatigue resistance are required. To meet such requirements, a PVA drawn yarn is twisted to produce a raw cord. In a general process for twisting synthetic fibers, an increase in twist number will result in a reduction in tenacity but an increase in fatigue resistance.

Thus, selecting suitable twist number according to the purpose of use is very important. For example, a tire cord used for carcass of a tire with 1500 d/2p is twisted to 300-500 TPM (turns per meter) before use.

[43] To enhance hot water resistance and fatigue resistance, the twisted PVA raw cord is crosslinked by the addition of a crosslinker.

[44] To infiltrate the crosslinker only into the non-crystalline region of the PVA fiber drawn to high draw ratio, the aromatic aldehyde is used as the crosslinker as described above.

[45] The aromatic aldehyde compound, which is used in the present invention, is preferably terephthalaldicarboxaldehyde (TDA). The crosslinking compound is used at the amount of 0.1-5 wt% relative to a fiber, and preferably 0.5-2.0 wt%. If it is used at the amount of less than 0.1 wt%, an insufficient heat water resistance below 130 °C will be caused, and if it is used at the amount of more than 5.0 wt%, a great reduction in tenacity will be caused to make the use of the high-tenacity tire cord difficult.

[46] To react the crosslinking compound with the OH group of PVA, an acid catalyst is required in an aqueous crosslinking solution. Although acids, such as sulfuric acid or acetic acid, may be used as the acid catalyst, the acetic acid is preferable in view of reaction rate adjustment and stability. The acid

catalyst is preferably used at the amount of 5-30 wt% relative to the aqueous crosslinking solution. If the acid catalyst is used at less than 5 wt%, crosslinking reaction will progress too slowly, and if it is used at more than 30 wt%, it will be difficult to remove the acid catalyst in a water-washing process after reaction.

[47] It is a key technical point in the present invention that crosslinking is performed with the addition of alcohol to the aqueous crosslinking solution containing the aromatic aldehyde compound and the acid catalyst. The addition of alcohol to the crosslinking solution allows significant prevention of a reduction in tenacity after crosslinking.

[48] Examples of preferred alcohols, which are added to the aqueous crosslinking solution in the present invention, include methanol, ethanol, propanol and butanol. Methanol is more preferred. The alcohol is added at the amount of 1-30 wt% relative to the aqueous crosslinking solution. At less than 1 wt%, a great reduction in tenacity will be caused during crosslinking to make the use for the high-tenacity tire cord difficult, and at more than 30 wt%, a cost disadvantage will be caused and also crosslinking will progress at a too slow rate.

[49] Another key technical point in the present invention is that a polyvinyl alcohol drawn yarn is plied into a 2-ply or 3-ply yarn to produce a raw cord wound on a bobbin for

crosslinking, and then, the raw cord wound on the bobbin for crosslinking is crosslinked by dipping it into the crosslinking solution.

[50] To infiltrate the crosslinking compound into the non-crystalline region of a PVA fiber having high crystallinity, a method is used in which the reaction solution is heated to 50 °C to increase the activity of the crosslinking compound, and a reactor is pressurized before use. Also, crosslinking time varies depending on the crosslinking compound and conditions, but is preferably longer than 30 minutes. However, if the crosslinking is performed for too long time, a great reduction in tenacity will be caused.

[51] The crosslinked PVA raw cord is washed and dried. To improve the adhesion to rubber, the dried raw cord is dipped in a RFL solution, dried and thermally treated. Concretely speaking, the dipping process is achieved by impregnating the fiber surface with a resin solution called resorcinol-formaline-latex (RFL), and this dipping process is performed in order to improve the problem of low adhesion to rubber of the tire cord fiber.

[52] The dipping solution, which is used for the adhesion between the PVA raw cord and rubber in the present invention, can be prepared by, for example, the following method. The following preparation example is given to more fully understand the present invention and is not intended to limit the present invention.

[53]	Resorcinol of 29.4 wt%	45.6 weight part
	Pure water	255.5 weight part
	Formalin of 37%	20 weight part
	Sodium Hydroxide of 10 wt%	3.8 weight part

[54] The solution prepared as described above is reacted at 25 °C for 5 hours with stirring, and then added with the following components.

[55]	VP-Latex of 40 wt%	300 weight part
	Pure water	129 weight part
	Ammonia water of 28%	23.8 weight part

[56] The solution containing the above components is aged at 25 °C for 20 hours, and maintained at a solid concentration of 19.05%.

[57] In order to prevent the RFL solution from infiltrating deeply into the inside of the fiber during the RFL dipping process, the raw cord is stretched to a stretch ratio of 0.5-3%, and a dip pick up (DPU) of the RFL is 3.0-9.0 wt%. At a stretch ratio of less than 0.5%, DPU will exceed 9 wt% so that the RFL solution will be infiltrated deeply into the inside of the staple fiber to reduce fatigue resistance. At a stretch ratio of more than 3%, excessive tension will be applied to the raw cord and thus will cause damages to the raw cord. Thermal treatment should be performed at a temperature of 170-230 °C, and preferably 200-220 °C where the movement of PVA molecules is the

best. By minimizing the tension applied to the fiber to allow for the greatest possible movement of the PVA molecules to maximize a heat treatment effect, the production of a treated high-tenacity PVA cord becomes possible. In a heat treatment process conducted after dipping the raw cord in the RFL solution, it is important that the dipped cord is maintained at a stretch ratio of 0 to -5%. If the stretch ratio in the heat treatment process is above 0%, when the dipped cord is used in a tire cord requiring high fatigue resistance, a cord cutting or separation phenomenon will occur which is due to low fatigue resistance below 60% resulting from the low elongation of the dipped cord. On the other hand, at a stretch ratio below -5%, molecular recrystallization in a vertical direction to the fiber axis will occur due to excessive molecular movement to cause a reduction in tenacity. If the crosslinker is present within the fiber not having been washed in the water-washing process after the crosslinking process, it acts as an impurity in a product where the PVA fiber was used. Thus, heat treatment is performed above 200 °C such that the remaining crosslinker can be reacted or volatilized to further improve crosslinking efficiency.

[58] Hereinafter, the bobbin for crosslinking used in the crosslinking as described above, and the use state thereof, will be described in brief.

[59] FIG. 1 is a perspective diagram showing the bobbin for crosslinking according to the present invention, and FIG. 2 is a use state diagram showing the use state of the bobbin for crosslinking according to the present invention.

[60] In the crosslinking as described above, a bobbin for crosslinking 10 is provided. The bobbin for crosslinking 10 comprises a first bobbin 10a forming one portion of the crosslinking bobbin 10, and a second bobbin 10b, which is detachably coupled to the first bobbin 10a and forms the other portion of the crosslinking bobbin 10. In the first and second bobbins 10a and 10b, hollows 16a and 16b are formed, respectively, a plurality of through-holes 13a and 13b are formed in the circumferential portion of the first and second bobbins so that cylindrical bobbin axes 12a and 12b on which a PVA raw cord is wound up are provided. In the inner end of the first and second bobbins 10a and 10b, a coupling protrusion 18a and a coupling groove 18b are formed which correspond to each other such that the second bobbin 10b is coupled to the first bobbin 10a.

[61] Herein, the first bobbin wheel 14a coupled to the first bobbin 10a serves to close the hollow 16a of the bobbin for crosslinking 10, and the second bobbin wheel 14b coupled to the second bobbin 10b serves to be connected with a crosslinker-feeding pipeline 30 in order to supply the crosslinker 2 into the inside of the PVA raw cord 1 wound on a bobbin for crosslinking

10 through a hollow 16a and 16b formed in a bobbin for crosslinking 10 by pressurizing or depressurizing with supplying apparatus by which crosslinker 2 is supplied in a specified pressure.

[62] In the crosslinking step, the bobbin for crosslinking 10 on which the PVA raw cord 1 was wound is provided in such a manner that it is dipped in a crosslinker 2 contained in a closed container 40 charged with the crosslinker 2. The crosslinker 2 is pressurized or depressurized to a specified pressure and supplied through a crosslinker-feeding pipeline 30. The supplied crosslinker is moved from inside to outside of the wound PVA raw cord 1 through the through-holes 13a and 13b formed in the respective bobbin axes 12a and 12b or moved from the outside to inside of the PVA raw cord 1, so that the inside and outside of the PVA raw cord 1 wound on the crosslinking bobbin 10 can be uniformly crosslinked.

BRIEF DESCRIPTION OF THE DRAWINGS

[63] FIG. 1 is a perspective diagram showing a bobbin for crosslinking according to the present invention.

[64] FIG. 2 is a use state diagram showing a crosslinker-introducing system using the bobbin for crosslinking according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[65] Hereinafter, the present invention is described in detail with referring to the following examples, but it is to be understood that the examples is solely for the purpose of illustration and do not limit the scope of the present invention. In the following examples, the estimating method and the measuring method as following is used.

[66] (a) tenacity(kgf) of PVA cord

[67] The tenacity of the filament is measured using low speed elongation tester, and the filament is tested after being dried at 107 °C for 2 hours. The filament is twisted by 80TPM(80turns/meter) and the length of the filament is 250mm and the elongation speed is 300m/min.

[68] (b) hot water resistance(WTb, °C)

[69] A twisted raw cord with 3,000 deniers is selected, cut into a 4-cm size, and then applied with a load of 3g/ply. The cord is dipped in water contained in a glass container for pressurization, and the temperature at which the fiber is broken is measured while elevating the temperature at a rate of 2 °C/minute.

[70] (c) fatigue resistance

[71] Samples were subjected a fatigue test using a Goodrich disc fatigue tester which is conventionally used for the fatigue test of tire cords. Then, they were measured for residual

tenacity, and fatigue resistances were compared. The fatigue test was conducted under the following conditions: 120 °C, 2,500 rpm, and 10% and 18% compression. After the fatigue test, the samples were submerged in tetrachloroethylene solution to swell rubber, and then, a cord was separated from the rubber and measured for residual tenacity. This residual tenacity was measured after drying at 107 °C for 2 hours using a conventional tensile strength tester by the above-described measurement method (a).

[72] Example 1

[73] PVA was used in a powder form with a degree of saponification of 99.9 mol% and a degree of polymerization of 2,000, and methyl alcohol and DMSO were used in a purified solvent mixture form with a water content of less than 100 ppm. To prepare the solvent mixture, DMSO and methyl were mixed such that the content of methyl alcohol content in the solvent was 5% by volume. PVA was dissolved in the solvent mixture such that it was 22 wt% relative to a PVA spinning dope. Next, the PVA solution was produced into a PVA fiber by a dry and wet spinning technique, using gel spinning. In this spinning process, a circular nozzle with a nozzle hole number of 500, a nozzle hole diameter of 0.5 mm and a L/D ratio of 5 was used. Also, air-gap was 50 mm, and methanol was used as a solvent in a coagulation bath. At this time, the coagulation bath was maintained at a

solvent/methanol mixing ratio of 20/80 and a temperature of 0 °C. After passing through an extraction tank, the PVA fiber must be free of the DMSO solvent. If the solvent remains in the filament, it is discolored in a thermal drawing process at high temperature to act as a main cause of deteriorating the physical properties of the final filament. In the thermal drawing process, two-step hot air heating was used in which the hot air heating temperature was 200 °C at the first step and 220 °C at the second step, and the draw ratio was adjusted such that total draw ratio was 13.5. As a result, a high-strength PVA fiber with a strength of 13.0 g/d and an elongation of 7.0% was produced. This drawn yarn was twisted to plying and cabling number of 300 TPM to produce a raw cord yarn having a tenacity of 34 kgf. The raw cord wound on a bobbin for crosslinking was crosslinked by dipping it in terephthalaldicarboxaldehyde (TDA) as aromatic aldehyde through a crosslinker-introducing apparatus capable of effectively inducing crosslinking. In the crosslinking reaction, 2 wt% of terephthalaldicarboxaldehyde (TDA) and 10 wt% of acetic acid were dissolved in water to prepare an aqueous crosslinking solution, and 10 wt% of methanol was added to the aqueous crosslinking solution, and then, the raw cord wound on the bobbin for crosslinking was crosslinked by dipping it in the aqueous crosslinking solution at 70 °C for one hour and washed with water. The crosslinked raw cord with tenacity of 33.6 kgf was

impregnated with a RFL solution to produce a treated PVA cord. The treated PVA cord was measured for its physical properties and the results are summarized in Table 1 below.

[74] Examples 2 and 3

[75] The ratio between terephthalaldicarboxaldehyde, acetic acid and methanol was adjusted to a ratio given in Table 1, and the resulting raw cord was crosslinked and then measured for its physical properties, including tenacity and fatigue resistance.

[76] Comparative Examples 1 and 2

[77] Comparative Example 1 is a non-crosslinked case and the results are given in Table 1, and Comparative Example 2 is a case where methanol was not used in the aqueous crosslinking solution. The results for Comparative Example 1 and 2 are given in Table 1.

[78] Comparative Examples 3 and 4

[79] In Comparative Example 3, crosslinking was performed for 6 hours and the results are given in Table 1. In Comparative Example 4, crosslinking was performed at 30 °C and the results are given in Table 1.

[80] Table 1

	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Concentration of TDA (wt %/aqueous solution)	2	2	2	-	5	2	2
Concentration of Acetic acid (wt %/aqueous solution)	10	10	15	-	10	10	10
Concentration of Methanol (wt %/aqueous solution)	10	5	10	-	-	10	10
Reaction temp. (°C)	70	70	70	-	70	70	30
Reaction time (min)	60	60	60	-	60	360	60
Tensile strength of drawn yarn (g/d)	13.5	13.5	13.5	13.5	13.5	13.5	13.5
Strength of raw cord (k g f)	34	34	34	34	34	34	34
Strength of treated raw cord (k g f)	33.6	32.8	32.1	-	21.2	28.2	33.4
Strength of dipped cord (k g f)	37.9	37.2	36.5	38	26.4	31.5	38.2
Fatigue resistance (%)	99	95	97	62	98	98	68
Hot water resistance(°C)	172	167	172	107	170	171	108

[81] As described above, the present invention provides the crosslinked raw cord which is produced by the method comprising the steps of: twisting a polyvinyl alcohol drawn yarn with 500-3,000 deniers to prepare a cabling yarn; plying the cabling yarn into a 2-ply or 3-ply yarn to prepare a raw cord; winding the raw cord on a bobbin for crosslinking; and crosslinking the raw cord wound on the bobbin for crosslinking, in an aqueous crosslinking solution containing an aromatic aldehyde compound and an acid catalyst, while adding alcohol to the aqueous crosslinking solution. The crosslinked raw cord has excellent hot water resistance, and thus, can be suitably used for tire cords.